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Passive microrheology simulations using stochastic particle methods

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Abstract

Passive microrheology is an experimental technique for the characterization of complex polymeric fluids based on the tracking of small embedded colloidal particles which undergo Brownian motion. Key modeling features for this flow problem include viscoelasticity of the suspending medium as well as the possibility to incorporate thermal fluctuations consistently. In this article some numerical methods suitable for the simulation of passive microrheology are reviewed. The so-called micro-macro approaches are based on the coupling between the continuum hydrodynamics description of the complex liquid with microscopic simulations of polymers using Brownian Dynamics. The advantage of using these methods is related to the consistent incorporation of thermal noise as well as the possibility to simulate microscopic polymer dynamics exactly. On the other hand, computational limitations are mainly due to the fact that in order to reproduce realistic conditions a large number of stochastic realizations is generally necessary. An alternative approach that bypasses the use of micro-macro models is represented by a Lagrangian particle method based on Smoothed Particle Hydrodynamics. In this method the viscoelasticity of the solvent is modelled via a continuum Oldroyd-B model whereas thermal fluctuations, inherently present at the microscopic scale, are incorporated into the particle framework by application of the GENERIC formalism, ensuring the strict fulfilment of the Fluctuation-Dissipation theorem. As an application, the particle method is used to simulate a realistic case in passive microrheology. In particular, a rigid structure suspended in the viscoelastic solvent is modeled and the rheological properties of the Oldroyd-B fluid, namely frequency-dependent storage and loss moduli, are extracted through the standard microrheological route, that is, by measuring the probe mean square displacement (MSD) and linking it to the solvent viscoelasticity by assuming the validity of a generalized Stokes-Einstein relation (GSER). Good agreement with the analytical theory for the Oldroyd-B model is observed only up to maximal frequencies corresponding to time scales considerably larger than the Brownian time of the probe particle where the diffusive regime is fully established. At larger investigated frequencies, a crossover between diffusive and ballistic behavior for the MSD of the probe is observed and validity of the GSER is questionable. The model presented here provides an optimal computational framework to complement experimental observations and to analyze quantitatively the basic assumptions involved in the theory of microrheology.

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Keywords: Smoothed Particle Hydrodynamics, multiscale micro-macro methods, viscoelasticity, thermal fluctuations, microrheology;

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1. Introduction

Microrheology is an experimental technique for the characterization of the rheology of complex fluids based on the tracking of small embedded colloidal particles [1, 2]. Since its introduction in [3] the technique has been expanded in several directions and the number of applications is continuously growing, from molecular liquids, polymers, DNA, to colloids, liquid crystals, biopolymers, and biological cells. As opposed to usual rheological measurements in which a macroscopic sample is placed in between solid moving walls, microrheology offers a number of advantages [1]. Among them, it does only need minuscule quantities (microliter) of the material, which is certainly an advantage when dealing with biological fluids, living cells or otherwise expensive materials. While the possibility of using externally forced probes in order to generate flows from which the rheological properties of the fluid could be extracted (active microrheology) was not new, the original idea in[3] was that the very *thermal motion* of an unforced Brownian particle could be used to probe the *viscoelasticity* of the medium (passive microrheology). This is possible after a crucial assumption is taken, the Generalized Stokes-Einstein relation (GSER), that links the velocity autocorrelation or root mean displacement of the Brownian particle with the complex shear modulus of the fluid. Although the GSER is just an empiricism, it has been justified from the classical viscous-viscoelastic analogy and is therefore generally valid whenever the assumptions implicit in the usual Stokes-Einstein relation hold. The conditions under which the GSER is valid have been carefully analysed in the review paper [2].

On the other hand, computer simulations represent an essential complementary tool for the investigation of complex fluids because they allow to switch on and off particular features at will, thus allowing for a differential understanding of the behavior of the entire system. However, from the computational point of view, the study of microrheology of complex polymeric fluids has been rather scarce. Microrheology simulations based on Dissipative Particle Dynamics (DPD) are restricted to situations where the polymers (modelled as long-chains of linked DPD particles) have typical contour lengths of the same order of the probe size [4]. This introduces strong heterogeneities in the local structure of the liquid near the probe with consequent violation of the continuum hypothesis for the the suspending medium [2]. A numerical method aiming at the study of the validity of the GSER in microrheology must rule out the previous scenario and ensure solvent homogeneity overall the fluid domain. This can be enforced in microscopic simulations only when a large scale separation exists between the colloidal probe size and the typical polymer contour length, therefore requiring to increase enormously the number of simulated particles and producing unacceptably large CPU time. The alternative way is to consider a continuum model for the solvent.

In this paper a particle-based method for microrheology simulations of complex solvent liquids modelled through an Oldroyd-B model is reviewed. The latter holds strictly for a suspension of long-chain molecules under dilute assumption, but more realistic constitutive equations can be easily incorporated in the present framework. By describing the solvent medium via a continuum partial differential equation, we implicitly assume homogenization over the characteristic size of the probe particle, namely its diameter is much larger than the size of the polymer molecules in suspension. There has been a recent interest in the simulation of particles immersed in viscoelastic fluids from a computational fluid dynamics point of view [5]. While these cited works may be of relevance to active microrheology, they cannot address issues of passive microrheology because Brownian fluctuations are not included. Indeed there are not many computational models that allow one to address *hydrodynamic fluctuations* of viscoelastic fluids, which are the ultimate responsible for the thermal motion of suspended particles [6]. Some exceptions are represented by so-called micro-macro approaches as the CONNFFESSIT method [7], the viscoelastic DPD extension of Ref. [8] or its thermodynamically consistent version [9]. The advantages of these approaches is the consistent incorporation of thermal noise as well as the possibility to simulate exactly microscopic polymer models. On the other hand, their main limitation is related to the fact that a large number of stochastic realizations must be considered, therefore limiting the total number of polymers to be simulated.

The fluid particle method reviewed in this paper for the simulation of viscoelastic fluids, being based on a continuum description, represents a numerically efficient alternative and, at the same time, allows for the introduction of thermal fluctuations in consistent way [10]. This particle model can be viewed as a Smoothed Particle Hydrodynamics (SPH) [11, 12] Lagrangian discretization of the Oldroyd-B model with proper introduction of the thermal noise.

In order to perform passive microrheology simulations a model for a rigid structure suspended in the medium needs to be embedded in the present framework. We follow here the ideas presented in [13] where a colloidal particle is modelled by freezing a number of SPH boundary particles within the solid domain. Thermal motion on the suspended

particle is implicitly induced by the thermal agitation of the viscoelastic solvent and does not need to be separately modelled. In order to validate our method, here we apply it to the case of a spherical particle suspended in a Brownian viscoelastic fluid and extract its diffusional properties, namely mean square displacement (MSD). Microrheology post-processing routines based on the procedure presented in [14] are therefore used to obtain frequency-dependent storage and loss moduli of the solvent from the MSD and the results are compared with the theory. The new model provides an optimal computational framework to complement experimental observations and to analyze quantitatively the basic assumptions involved in the theory of microrheology.

The paper is organized as follows. In Sec. 2 some micro-macro approaches for the modeling of viscoelastic fluids with thermal fluctuations are described. In Sec. 3 the SPH-based viscoelastic particle model for the solvent is presented and its deterministic/stochastic equations discussed. In Sec. 4 the numerical results are presented: advantages and limitations of the present approach are discussed. Finally, in Sec. 5 conclusions are reported.

2. Mesoscopic viscoelastic models based on micro-macro approach

A possible approach for the description of complex viscoelastic fluids with thermal fluctuations comes from the direct application of so-called micro-macro approaches. The main idea behind these models is to couple a continuum hydrodynamics description of the conservation equations with a microscopic description of the micro-structural dynamic, in this case the polymers.

In order to illustrate this approach in some detail, let us consider the general Navier-Stokes equation written in Lagrangian form and equipped with the usual extra stress tensor introducing elastic effects

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\rho}\nabla p + \frac{1}{\rho}\nabla\cdot\tau^{v} - \frac{1}{\rho}\nabla\cdot\tau^{p}, \tag{1}$$

where $\tau^{v} = \eta_s(\nabla\mathbf{v} + \nabla\mathbf{v}^T)$ is the viscous stress tensor, η_s the solvent viscosity and τ^{p} is the polymeric contribution to the total stress tensor. Challenging is the evaluation of the components of τ^{p} at $(\mathbf{x},t)$. Microscopically, a dilute polymer solution (polymers dissolved in Newtonian solvent) is typically modeled by non-interacting dumbbells consisting of two beads connected with a spring and subjected to a dissipative force with friction coefficient ζ plus a stochastic contribution. Each dumbbell is described in terms of its orientation and length, i.e., by a vector $\mathbf{Q}$ connecting two beads. The evolution equation for the configuration distribution function (CDF) $\psi(\mathbf{x},\mathbf{Q},t)$ for dumbbells in dilute solution follows from standard kinetic theory for this problem and reads

$$\frac{d\psi}{dt} = -\frac{\partial}{\partial Q}\cdot\left(\kappa\cdot\mathbf{Q} - \frac{2}{\zeta}\mathbf{F}(\mathbf{Q})\right)\psi - \frac{2k_BT}{\zeta}\frac{\partial^2}{\partial\mathbf{Q}^2}\psi\,, \tag{2}$$

where k_B is Boltzmann's constant, T is the kinetic temperature and $\psi(\mathbf{x},\mathbf{Q},t)d\mathbf{Q}$ represents the probability of having a dumbbell located in $\mathbf{x}$ with a connector vector in the range $[\mathbf{Q}-d\mathbf{Q},\mathbf{Q}+d\mathbf{Q}]$. Equation (2) describes convection and diffusion of the CDF $\psi(\mathbf{x},\mathbf{Q},t)$ subjected to the (transposed) macroscopic deformation rate tensor $\kappa(\mathbf{x},t) = (\nabla\mathbf{v}(\mathbf{x},t))^T$ and $\mathbf{F}(\mathbf{Q})$ represents the spring force acting between bonded beads. In order to recover the extra stress tensor τ^{p} the Kramer's expression for the stress tensor can be used

$$\tau^{p} = -nk_BT\,\mathbf{1} + nH\langle\mathbf{F}(\mathbf{Q})\mathbf{Q}\rangle, \tag{3}$$

where n is the number density of dumbbells, and $\mathbf{1}$ the unit tensor. The average of a quantity $f(\mathbf{Q})$ is defined via $\langle f\rangle = \int\psi f(\mathbf{Q})d\mathbf{Q}$. The problem, Eq. (1), supplemented with Eqs. (2)-(3), is therefore well-defined once the initial conditions for the macroscopic velocity field $\mathbf{v}(\mathbf{x},t_0)$ and for the microscopic CDF $\psi(\mathbf{x},\mathbf{Q},t_0)$ are known. By integrating Eq. (2) we obtain a new CDF ψ, when introduced in Eq. (3), produces a new extra stress tensor field $\tau^{p}(\mathbf{x},t)$ for the momentum equation, thus closing the loop. Despite of its apparent simplicity, the described way to proceed poses many computational problems. In fact, Eq. (2) is a second-order partial differential equation with derivatives in both configurational and physical space. Consequently, it should be integrated on a high-order dimensional space (6 in the 3D case) which makes this approach generally quite demanding.

An alternative approach is provided by stochastic micro-macro methods (e.g. CONNFFESSIT [7, 15]). The goal here is to evaluate a solution of the exact kinetic equation (2) in a way which permits to avoid the computational

bottleneck caused from its numerical discretization on the high-order configurational space and at the same time to incorporate fluctuations in the polymeric stress consistently. The main idea is based on a stochastic evaluation of the CDF of the dumbbells ψ instead of its determination based on Eq. (2). Use is made of the fact, that the Fokker-Planck equation (2) has an equivalent formulation in terms of a stochastic Markovian process (Langevin equation). To be more specific, if we consider a set of N_p dumbbells $\{\mathbf{Q}_1, \mathbf{Q}_2, .., \mathbf{Q}_{N_p}\}$ distributed over the domain, the resulting equivalent formulation of Eq. (2) reads

$$d\mathbf{Q}_k(t) = \left(\kappa(t)\cdot\mathbf{Q}_k(t) - \frac{2}{\zeta}\mathbf{F}(\mathbf{Q}_k(t))\right)dt + \sqrt{\frac{4k_BT}{\zeta}}d\mathbf{W}_k(t), \tag{4}$$

which represents the Îto stochastic differential equation for each individual dumbbell $k = 1, ..., N_p$. The quantities $d\mathbf{W}_k$ denote N_p independent stochastic Wiener processes. The set of dumbbell elongation vectors evolve at every time step following Eq. (4). This procedure constitutes the Brownian Dynamics method (BD). The extra stress tensor is calculated by applying Kramer's expression (3) to the new set of dumbbell variables, i.e., $\tau^p = -nk_BT\mathbf{1} + nN_p^{-1}\sum_{k=1}^{N_p}\mathbf{F}(\mathbf{Q}_k)\mathbf{Q}_k$. Finally, as discussed above, the polymeric stress enters into the macroscopic flow calculation via Eq. (1). The advantages of this approach is the consistent incorporation of thermal noise as well as the possibility to simulate exactly complex dumbbell forces $\mathbf{F}(\mathbf{Q})$. On the other hand, the main limitation is related to the fact that N_p stochastic evolution equations for the independent dumbbell realizations must be solved for every fluid element discretizing the momentum equation (1) , therefore allowing either for a rather small number of dumbbells or small number of spatial elements compared to real situations. In the following of this paper a stochastic particle model which allows to incorporate thermal fluctuations consistently on the top of a continuum model for Hookean dumbbells is reviewed. As it will be clear later, the main advantage is the possibility to evolve only few degrees of freedom per fluid element (compared to $N_p \gg 1$). The drawback is that the method still relies on an simple Oldroyd-B constitutive equation and it is therefore restricted to the dynamics of Hookean or approximated FENE dumbbells models.

3. The mesoscopic viscoelastic particle model

In this section an alternative SPH-based particle model for the simulation of viscoelastic solvent with thermal fluctuations [10] is presented. The framework is based on a continuum description whereas thermal fluctuations are consistently included enforcing the Fluctuation-Dissipation theorem.

The isothermal fluid is represented by a set of N fluid particles of mass m. For a Newtonian fluid [16], the state of the system is given by the position $\mathbf{r}_i$, velocity $\mathbf{v}_i$ associated to each fluid particle i. The elastic behavior of the viscoelastic fluid is obtained by assuming that every fluid particle i contains N^p polymer molecules. In this model, every molecule is represented by two beads joined with a Hookean spring. The general configuration of the N_p polymer molecules within the fluid particle is described by a conformation tensor $\mathbf{c}_i$ defined as

$$\mathbf{c}_i = \frac{1}{N_p Q_{eq}^2}\sum_{k=1}^{N_p}\mathbf{Q}_k\mathbf{Q}_k \tag{5}$$

which contains all the information about their average orientation/extension. Q_{eq}^2 represents the average squared dumbbells equilibrium extension. The GENERIC formalism allows one to obtain the evolution for the conformation tensor coupled with the dynamics of the rest of variables $\mathbf{r}_i, \mathbf{v}_i$ in a thermodynamically consistent way [10].

3.0.1. Deterministic equations

The deterministic evolution of the position, velocity of every fluid particle reads [10]

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt, \\ m d\mathbf{v}_i|_{\text{det}} &= \left[\sum_j\left(\frac{\Pi_i}{d_i^2}+\frac{\Pi_j}{d_j^2}\right)\mathbf{r}_{ij}F_{ij} - \frac{5\eta_s}{3}\sum_j\frac{F_{ij}}{d_i d_j}\left(\mathbf{v}_{ij}+\mathbf{e}_{ij}\left(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij}\right)\right)\right]dt \end{aligned} \tag{6}$$

where summations are made over all the fluid particles j located in the neighborhood of particle i. Π_i is the total reversible stress tensor associated to the i-th particle. The viscous stress tensor in Eq.(1) is modelled by the second

term in Eq. (6) involving the solvent viscosity η_s. $\mathbf{e}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ is the unit vector joining particles i and j, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is their relative velocity The geometric factor F_{ij} and the number density d_i of the fluid particle i are defined as [17] and read $F_{ij} = -\frac{\nabla W(r_{ij},r_c)}{r_{ij}}$ and $d_i = \frac{1}{\mathscr{V}_i} = \sum_j W(r_{ij},r_c)$, where $\mathscr{V}_i$ is the volume of the i-th fluid particle, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between particles i and j, $W(r_{ij},r_c)$ is a kernel function and r_c its cutoff radius. In this work a quintic spline kernel is used [12]. The previous equations correspond to the standard Lagrangian discretization of the hydrodynamic equations used in the Smoothed Particle Hydrodynamics method (SPH) [11].

The velocity gradient tensor for particle i is defined as $(\nabla \mathbf{v})_i = \frac{1}{d_i}\sum_j F_{ij}\mathbf{r}_{ij}\mathbf{v}_{ij}$. In the case of a simple Newtonian fluid the pressure tensor reads $\Pi_i = \mathbf{1}P_i^s$ where $\mathbf{1}$ is the unit tensor and P_i^s is the scalar solvent pressure which can be modelled by the following equation of state relating it to the local mass density $\rho_i = md_i$: $P_i^s = c^2(\rho_i - \rho_0)$, where ρ_0 is a reference density and c is the solvent speed of sound which might be chosen based on a scale analysis [12] so that the density variation is less than a given value (weakly-compressible approximation).

Note that velocity change of the fluid particles has a reversible part, given by the gradient of the pressure tensor, and a irreversible viscous part that is modelled as a friction force between the fluid particles that decreases their relative velocities.

With the previous definition of pressure tensor, Eqs. (6) correspond to a SPH Lagrangian discretization of the Navier-Stokes equations [16] for a compressible isothermal Newtonian fluid.

To incorporate viscoelastic effects the definition of the pressure tensor Π_i needs to be modified in order include the conformation tensor $\mathbf{c}_i$. In the case of a set of Hookean dumbbells, it reads [10]

$$\Pi_i = \mathbf{1}P_i^s + \tau_i^p = \mathbf{1}P_i^s + \mathbf{1}P_i^{\mathrm{osm}} - n_i^p k_B T_i \mathbf{c}_i \tag{7}$$

where $n_i^p = N^p/\mathscr{V}_i$ is the polymer concentration of the i-th particle, $P_i^{\mathrm{osm}} = n_i^p k_B T_i$ its osmotic pressure and k_B the Boltzmann constant. In absence of thermal fluctuations, the conformation tensor evolves according to the following equation

$$\dot{\mathbf{c}}_i = \mathbf{c}_i \cdot \kappa_i^{\mathrm{T}} + \kappa_i \cdot \mathbf{c}_i + \frac{1}{\tau}(\mathbf{1} - \mathbf{c}_i) \tag{8}$$

where $\kappa_i = (\nabla \mathbf{v})_i^T$ is the transposed of the velocity gradient tensor. The first two terms of the equation are reversible and represent the advection of the conformation tensor with the flow. The last one is irreversible and makes the conformation tensor to tend to its relaxed state which is given by the unit tensor. This happens on a time scale governed by the polymer relaxation time τ. The above set of equations for the viscoelastic fluid particles can be understood as a Lagrangian discretization of the well-known Oldroyd-B viscoelastic model for dilute polymeric solutions [10].

3.0.2. Stochastic equations

When suspended structures have submicron size, thermal fluctuations start playing an important role. The introduction of thermal fluctuations in conventional computational fluid dynamics models is not a trivial matter, because of the subtle interplay between the discretization procedure and the necessary strict fulfilment of the Fluctuation-Dissipation theorem. For physically motivated fluid particle models of the kind proposed in [16, 10] the task is, however, rather simple. In that case, thermal fluctuations are represented by noise terms $d\tilde{\mathbf{v}}_i$ and $d\tilde{\mathbf{c}}_i$ in the evolution of the velocity and conformation tensor of the fluid particles. The noise in the conformation tensor variable is assumed to be statistically independent of the velocity noise terms. The latter are the same as in the model for Newtonian fluid [16]:

$$md\tilde{\mathbf{v}}_i = \sum_j A_{ij} d\hat{\mathbf{W}}_{ij} \cdot \mathbf{e}_{ij} \tag{9}$$

where $d\hat{\mathbf{W}}_{ij} = \frac{1}{2}\left[d\mathbf{W}_{ij} + d\mathbf{W}_{ij}^T\right]$ is the symmetric part of $d\mathbf{W}_{ij}$, which is a matrix of independent increments of the Wiener process associated to the particle pair i, j. The amplitudes A_{ij} of the noise terms are given by

$$A_{ij} = \left(\frac{40\eta_s}{3} k_B \frac{T_i T_j}{T_i + T_j} \frac{F_{ij}}{d_i d_j}\right)^{1/2} \tag{10}$$

The complete dynamics of the particle positions, velocities are therefore obtained from Eqs. (6) and (9) as

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt, \\ m d\mathbf{v}_i &= m d\mathbf{v}_i\big|_{\rm det} + m d\tilde{\mathbf{v}}_i, \end{aligned} \tag{11}$$

Concerning the stochastic evolution of the conformation tensor, as discussed in detail in [10], it is convenient to evolve directly its eigenvalues λ_α and eigenvectors $\mathbf{u}_\alpha$ ($\alpha = 1,2,3$) (sub-indexes referring to fluid particles are suppressed to simplify the notation) rather than the tensor components themselves. The evolution of the eigenvalues and eigenvectors can be obtained from the dynamic equation (8) with the addition of thermal fluctuations with the result

$$\begin{aligned} d\lambda_\alpha &= 2\lambda_\alpha \kappa_{\alpha\alpha} dt + \frac{2}{\tau}[1-\lambda_\alpha]\, dt + \frac{2}{\tau N^p} dt + \left(\frac{4\lambda_\alpha}{\tau N^p}\right)^{\frac{1}{2}} d\tilde{\lambda}_\alpha \\ \dot{\mathbf{u}}_\alpha &= \sum_{\beta\neq\alpha} H_{\alpha\beta}\mathbf{u}_\beta \end{aligned} \tag{12}$$

where $\kappa_{\alpha\beta} = \mathbf{u}_\alpha \cdot (\nabla \mathbf{v})^T \cdot \mathbf{u}_\beta$ and

$$H_{\alpha\beta} = \begin{cases} \frac{1}{(\lambda_\alpha - \lambda_\beta)}\left[\lambda_\alpha \kappa_{\beta\alpha} + \lambda_\beta \kappa_{\alpha\beta}\right] & \text{if } \lambda_\alpha \neq \lambda_\beta \\ 0 & \text{if } \lambda_\alpha = \lambda_\beta \end{cases}$$

and where $d\tilde{\lambda}_\alpha$ are independent increments of the Wiener process, with the following variance $d\tilde{\lambda}_\alpha d\tilde{\lambda}_\beta = \delta_{\alpha\beta} dt$ The equations (11) and (12) can be understood as a discretization of the Oldroyd-B model equations with thermal noise consistently incorporated and correct thermodynamic scaling [18], [10].

Rigid objects as suspended solid particles are represented in this model following the ideas presented in [13]. Once a given object geometry is prescribed, particles can be placed inside the solid domain and regarded as boundary particles, which will interact with the fluid ones through the same standard forces presented in Eqs.(6)-(9). In order to perform these pairwise interactions, hydrodynamic variables must be assigned to the boundary particles. This is done by requiring specific boundary conditions to be satisfied at the interface. For example, the no-slip velocity condition on the arbitrary liquid-solid interface is automatically enforced if a suitable artificial velocity is temporally assigned to every boundary particle during the pairwise interaction. This velocity can be obtained by interpolation from the known value on the fluid particle assuming an instantaneous translational velocity of the solid object $\mathbf{V}_C$ on the nominal moving surface [13]. Once all pairwise interactions involving a boundary particle have been calculated, a total force exerted by the overall surrounding solvent particles on the entire solid object is obtained by summing the boundary contributions and its translational acceleration evaluated as $\mathbf{a}_C = \mathbf{F}_C/M$ where M is its total mass. Finally, the position $\mathbf{R}_C$ and velocity $\mathbf{V}_C$ of the solid particle are updated by time integration. As shown in [13], torques and rotation of the solid structure can be modelled analogously. In the microrheology simulations presented in this work, a freely-translating, non-rotating spherical solid particle will be considered.

4. Simulations

4.1. Equilibrium fluctuations

Associated to the stochastic differential equations (11) there exist a mathematically equivalent Fokker-Planck equation (FPE). The equilibrium solution of this FPE gives the Einstein equilibrium distribution function for the eigenvalues:

$$P(\lambda_\alpha) = \frac{1}{\mathscr{N}} \lambda_\alpha^{N^p/2} \exp\left\{-\frac{N^p}{2}\lambda_\alpha\right\} \tag{13}$$

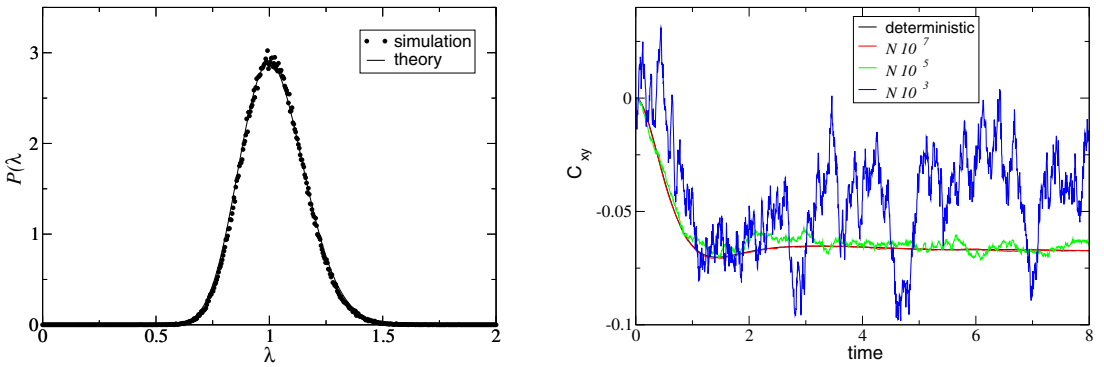

Fig. 1. Left: Equilibrium histogram of eigenvalues of the conformation tensor compared with the theoretical result in Eq. (13). Right: Time evolution of the off-diagonal component of the configuration tensor in a start up from rest of a Kolmogorov flow. For a given size of fluid particles, the evolution of the configuration tensor depends strongly on the number N^p of polymer molecules that are within the fluid particle. Few polymer molecules imply large fluctuations.

It is apparent that the width of this distribution function narrows with increasing number N^p of polymers within a fluid particle. In general, for a fixed *concentration* of polymers, the number N^p of polymer molecules will increase with the size of the fluid particles. As a consequence, the effect of thermal fluctuations in the configuration tensor (and, therefore, in the rest of the dynamics) will be reduced as the fluid particles are larger. The effect of switching off thermal fluctuations by using larger fluid particles has been discussed recently in the SDPD model for Newtonian fluids [18]. A simulation of Eqs. (11-12) is run in an equilibrium state (no forcing in a periodic box). We have binned the values of the eigenvalues realized during the simulation and computed the histogram in Fig. 1(left). The agreement with Eq. (13) is excellent.

4.2. Kolmogorov flow

To illustrate the advantage of the new stochastic formulation, we consider an inhomogeneous bulk shear given by the periodic Kolmogorov flow. A sinusoidal external forcing of a bulk fluid with an acceleration given by $\mathbf{g} = g_0(\sin ky, 0)$ is imposed where g_0 is the amplitude of the acceleration, and $k = 2\pi/L$. The fluid particles are accelerated by the external perturbation and eventually, after transient they achieve a steady state. In Fig. 1 (right) the stochastic time evolution of the component $\mathbf{c}^{xy}$ in the start up from rest of the Kolmogorov flow, for different number N^p of polymer molecules within the fluid particle is shown. As the number of polymer molecules is increased, the fluctuations in the configuration tensor decrease accordingly, in agreement with basic Statistical Mechanics principles. However, in microscopic conditions as those represented by microrheology, such fluctuations cannot be neglected and play a crucial role in the dynamics.

Note that, compared to the $3 \times N_p$ stochastic realizations needed (in three dimensions) for a micro-macro approach based on Brownian Dynamics integration of Eq. (4), here only 3 stochastic equations for the eigenvalues plus 9 determistic equations for the components of the eigenvectors are needed, independent on N_p which is here a simple input parameter. Considering that in realistic situations the number of polymers within every continuum element of fluid is $N^p \gg 1$, the computational benefit of the present approach is substantial.

4.3. Passive microrheology

In order to assess the validity of the proposed SPH-based particle model for the simulation of passive microrheology, in this section we extract the rheological properties of a model viscoelastic Oldroyd-B fluid for which the behavior is known, via the microrheology route commonly used in experiments. In particular, by recording the thermal motion

of a suspended solid spherical probe particle, its mean square displacement can be evaluated and the rheological properties of the surrounding solvent medium inferred. Results are compared to analytical solution for the Odroyd-B model

$$\overline{G}'(\overline{\omega}) = \frac{\overline{\omega}^2}{\overline{\omega}^2+1} \qquad \overline{G}''(\overline{\omega}) = \overline{\omega}\left(\frac{1}{\overline{\omega}^2+1}+\frac{\beta}{1-\beta}\right) \tag{14}$$

where $\overline{G}'$ and $\overline{G}''$ are the dimensionless storage and loss moduli, obtained by dividing G' and G'' by $n^p k_B T$.

The dimensionless frequency is defined as $\overline{\omega} = \omega\tau$, where τ is the elastic relaxation time. Note the total viscosity for the Oldroyd-B model is given by $\eta = \eta_s + \eta_p$ where $\eta_p = n^p k_B T \tau$ is the polymeric contribution. The dimensionless parameter $\beta = \eta_s/\eta$ appearing in the equation above characterizes the viscoelasticity of the fluid: namely $\beta = 0$ for a purely elastic liquid whereas $\beta = 1$ for a purely viscous fluid.

In this section we extract the storage and loss moduli of the suspending Oldroyd-B through the *passive microrheology route*. Consistency requires to obtain the analytical rheological behavior known for the Oldroyd-B fluid. Discrepancy between the results provides information about the failure of approximations involved in the theory of microrheology [2].

In order to link solvent viscoelasticity to the root mean square displacement of the probe particle, the Generalized Stokes-Einstein Equation [3] is generally assumed

$$\tilde{G}(s) = \frac{k_B T}{\pi R s \left\langle \triangle \tilde{r}^2(s) \right\rangle} \tag{15}$$

where R is the radius of the probe. Numerically demanding Laplace transforms of the data are avoided by using the method proposed recently in [14]. Here the rheological parameters of the fluid are obtained from compliance measurements. The complex compliance $J(\omega)$ is related to the complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ through $J(\omega) = 1/(i\omega G^*(\omega))$ [14]. Therefore, the compliance in the time domain (denoted as $j(t)$) is related to the mean square displacement of the Brownian particle through $j(t) = \frac{3\pi R}{dk_B T}\left\langle \triangle r^2(t) \right\rangle$ where d is the number of dimensions.

4.3.1. Simulation parameters

Three-dimensional simulations of a spherical Brownian particle suspended in a viscoelastic solvent are performed. Units and parameters are selected in such a way that the Boltzmann constant and the temperature are $k_B = 1$, $T = 1$. The radius of the colloidal particle is $R = 1$ and its density is the same as the solvent density $\rho = 1$ (neutrally buoyant condition). The length of the cubic periodic box is $L = 7.5$ corresponding to a number of SPH particles $N_x = N_y = N_z = 30$. Concerning the colloidal particle, it is represented by approximately 270 boundary particles corresponding to 4 particles along its radius. The polymers concentration is $n_p = 640$. Based on the previous parameters, the following characteristic time scales can be defined $t_s = \frac{R}{c} \longrightarrow$ Sonic time, $t_\nu = \frac{R^2\rho}{\eta} \longrightarrow$ Viscous time, $t_{br} = \frac{M}{6\pi\eta R} = \frac{2}{9}t_\nu \longrightarrow$ Brownian time, $\tau = \frac{(1-\beta)\eta}{n_p k_B T} \longrightarrow$ Elastic time, $t_D = \frac{R^2}{D} = \frac{6\pi\eta R^3}{k_B T} \longrightarrow$ Diffusion time. Here t_s corresponds to the time spent by a sound wave to propagate over a distance R, t_ν is the time of diffusion of fluid momentum over the same distance and t_D corresponds to the diffusion of mass; t_{br} is the Brownian time corresponding approximately to the decay of the autocorrelation function of the colloid velocity and τ the elastic time. Based on realistic values, the following hierarchy of time scales should hold $t_s \ll t_{br} < t_\nu \ll t_D$: the first inequalities ensures a quasi-incompressible flow of the solvent liquid whereas the last one a diffusion of momentum much faster than the mass.
In polymer solutions the elastic time τ corresponds to the longest relaxation time of the polymer (decay of the end-to-end radius autocorrelation) and might be smaller or larger than t_D depending on the polymer contour length and concentration.

4.3.2. Numerical results

The results for these simulations are reported in Fig. 2 and compared with the theoretical solutions given in Eq. 14. We can see that the agreement for both the storage and loss moduli is excellent over about two orders of magnitudes in

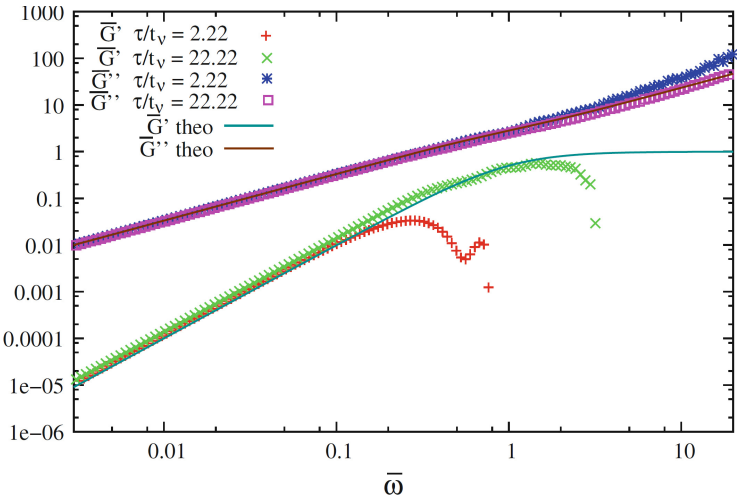

Fig. 2. Viscous and elastic moduli for the viscoelastic Oldroyd-B fluid with $\beta = 0.5$ obtained from the passive microrheology simulations. Lines denote theoretical results.

the frequency. Deviations from the theory start to appear due to the fact that the typical time scales investigated become very small and start to be comparable with the dimensionless viscous time $\bar{\tau_v} = \tau_v/\tau$ where the diffusive regime is not established. In both graphs, it can be observed, as expected, that an increment of the ratio between elastic and viscous times of ten times, enlarges of about one order also the range of frequencies where accurate microrheology results are extracted. We have explicitly checked that appreciable deviations in the results with the theory appear always at a threshold time scale $t = 1/\omega \sim 10\tau_v$. For smaller lapse times, crossover between ballistic regime and diffusive regime occurs, fluid inertia effects start to be important and the application of GSER is questionable. The regime studied here could be particularly interesting for the extension of standard microrheology towards *passive nanorheology* measurements where the effect of ballistic motion and solvent inertia play a crucial role.

5. Conclusions

The study of the passive microrheology of polymeric fluids represents a challenging task for numerical simulations. There are not many computational models that allow to address *hydrodynamic fluctuations* of viscoelastic fluids, which are the ultimate responsible for the thermal motion of suspended probe particles. In this paper we have reviewed multi-scale micro-macro approaches based on the coupled solution of continuum hydrodynamic equations together with a BD-based solution for a set of stochastic realizations of polymers. The advantages of these approaches is the consistent incorporation of thermal noise as well as the possibility to simulate exactly complex dumbbell models based, for example on microscopic FENE forces. On the other hand, the main computational limitation is related to the fact that a large number N_p of stochastic evolution equations must be solved for every discrete fluid element.
In the attempt to solve this drawback, a SPH-based stochastic particle model which allows to incorporate thermal fluctuations consistently on the top of a continuum model for Hookean dumbbells has been recently presented. The method allows to consider only few degrees of freedom per fluid particle , reducing substantially the overall algorithmic complexity. As application of the present approach, passive microrheology simulations can be performed effectively and the basic approximations behind the theory quantitatively analyzed. In particular this model can be used to validate novel GSER relations which might be able to extend the current use of microrheology to larger frequencies.

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